DIELECTRIC ABSORPTION OF AND INTERNAL ROTATION IN ANISOLES AND SUBSTITUTED ANISOLES IN SOLUTIONS IN NON-POLAR SOLVENTS

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ABSTRACT. The dielectric loss due to absorption of microwaves of frequency 38.8 KMc/s in dilute solutions of anisoles and some substituted anisoles in a number of non-polar solvents at different temperatures (T) have been investigated. It has been found that under the assumption of a single relaxation time (τ) the plots of log (τT) against $1/T$ for the solutions of *o*-chloro- *o*-bromo-, *o*-nitro- and *p*-chloroanisoles in paraffin, *n*-hexane, CCl_4 and benzene, are linear while in the case of anisole solutions, such plots are *s*-shaped curves, showing thereby existence of more than one relaxation time. The observed results in this case have been analysed under the assumption of two relaxation times τ_1 and τ_2 the former due to rotation of the molecule as a whole and the lattter due to rotation of the methoxy group. The analysis shows that the percentage contribution to the overall loss due to the rotation of the methoxy group is about 10% in paraffin solution and about 30% in hexane solution. This percentage is still higher in benzene and CCl_4 solutions. The value of τ_2 in paraffin and hexane solutions at about 275°K is about 4×10^{-12} sec with a potential barrier of 4.3K.Cal/mole. This value of τ_2 in benzene and CCl_4 occurring at about 295°K seems to be consistent with experimental results. The values of τ_1 due to rotation of the molecule as a whole in the case of anisole in all these cases are compatible with those observed for rigid dipolar molecules of similar size under similar circumstances.

INTRODUCTION

The phenomenon of dielectric relaxation of polar molecules in the liquid state and in solutions in non-polar solvents has been extensively studied both theoretically and experimentally. The agreement between the two has been found to be fairly satisfactory in the case of polar molecules with rigid dipoles but in the case of molecules with polar groups, having the possibility of rotational motions the agreement is not satisfactory.

From considerations of rotational Brownian motion of the different polar groups attached to the polar molecule, Budo (1938), following Debye, showed that in general a number of different relaxation times characteristic of the different polar groups and of the whole molecule are to be expected, in contrast to a single relaxation time observed in the case of rigid dipolar molecules. He also showed that the relative contributions by various polar groups to the overall dielectric loss will be proportional to the square of the ratios of the partial moments of the

respective groups to the moment of the whole molecule. Many workers have experimentally investigated the dielectric loss of such molecules but their experimental findings differ widely amongst each other. As, for example, in the case of solution of methoxy benzene in benzene at 20°C, the time of relaxation of the OCH_3 group have been reported as varying from 7×10^{-12} sec to 0.8×10^{-12}sec., while the percentage contribution to the overall loss due to the methoxy group varies from 80% to about 20% (Hase, 1953; Fisher, 1954; Klages, 1954; Grubb *et al*, 1961; Klages *et al*, 1961; Forest *et al*, 1964).

Because of this wide divergence in the results reported by various workers, an investigation of the dielectric behaviour of anisole and some substituted anisoles dissolved in some non-polar solvents at different temperatures was undertaken. An analysis of the results of the investigation has been presented in this paper.

EXPERIMENTAL

Anisole, *o*-chloro-, *o*-bromo-, *o*-nitro- and parachloro anisoles studied in the present investigation were of chemically pure quality. These were fractionated and the proper fractions were distilled under reduced pressure and dried before being used in the investigations. The solvents carbon tetrachloride, benzene, *n*-hexane and medicinal paraffin were dried by usual method. The dried solvents showed slight losses in the 38.8 Kmc/s frequency region, which were properly taken into account in determining the overall losses due to the various solutions. The experimental arrangement and method of calculation of loss tangent (tan δ) were the same as described earlier (Bhattacherjee *et al*, 1964).

THEORY OF THE METHOD

Following Budo (1938), the average dipole moment of anisole or the para substituted anisole in a high frequency electric field of angular frequency ω is given by

$$(\mu)_{av} = \left\{ \frac{\mu_1^2}{1+j\omega\tau_1} + \frac{\mu_2^2}{1+j\omega\tau_2} \right\} \frac{E_0 e^{j\omega t}}{3kT} \qquad \ldots (1)$$

where μ_1 is the dipole moment along the C-O bond, the axis of rotation of the methoxy group and τ_1 is the relaxation time for the orientation of the whole molecule, μ_2 is the moment component perpendicular to the axis of rotation and τ_2 is the relaxation time associated with it. If the moment μ_g of the methoxy group is inclined at an angle ϵ to the axis of rotation then $\mu_2 = \mu_g \sin\epsilon$ and μ_1 is composed of the moments $\mu_g \cos\epsilon$, μ_a- the moment of the atom in the para position and some contribution from the mesomeric structures (Grubb *et al*, 1961). This will be the average moment if in all the molecules the methoxy group is free to rotate. However, if only the fraction t is capable of rotation

(Fischer, 1964; Klages *et al*, 1961) the fraction $(1-t)$ will relax in the field as rigid molecules and the average moment will be modified as

$$(\mu')_{av} = \left\{ \frac{(1-t)\mu^2}{1+j\omega\tau_1} + t\left(\frac{\mu_1^2}{1+j\omega\tau_1} + \frac{\mu_2^2}{1+j\omega\tau_2} \right) \right\} \frac{E_0 e^{j\omega t}}{3kT}$$

$$= \left\{ \frac{\mu^2 - t(\mu^2-\mu_1^2)}{1+j\omega\tau_1} + \frac{t\mu_2^2}{1+j\omega\tau_2} \right\} \frac{E_0 e^{j\omega t}}{3kT} \qquad \ldots (2)$$

Remembering that the observed dipole moment μ is given by $\mu^2 = \mu_1^2+\mu_2^2$ equation (2) gives

$$(\mu')_{av} = \left(\frac{\mu^2 - t\mu_2^2}{1+j\omega\tau_1} + \frac{t\mu_2^2}{1+j\omega\tau_2} \right) \cdot \frac{E_0 e^{j\omega t}}{3kT}$$

$$= \left(\frac{C_1\mu^2}{1+j\omega\tau_1} + \frac{C_2\mu^2}{1+j\omega\tau_2} \right) \frac{E_0 e^{j\omega t}}{3kT} \qquad \ldots (3)$$

where $$C_1 = 1 - \frac{t\mu_2^2}{\mu^2}, \quad C_2 = \frac{t\mu_2^2}{\mu^2} \text{ and } C_1+C_2 = 1 \qquad \ldots (3a)$$

Combining this expression with Debye expression for tan δ in the case of very dilute solutions in non-polar solvents, we obtain

$$\tan\delta = \frac{(\epsilon'+2)^2}{\epsilon'} \cdot \frac{4\pi N\mu^2 c}{27kT}\left(\frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1+\omega\tau_2^2} \right) \qquad \ldots (4)$$

ϵ' is dielectric constant of the solution at the frequency of the applied field and all other constants having their usual significance. When the concentration c is small $\epsilon' \to \epsilon_0$ the static dielectric constant of the solvent. Eqn. (4) then gives

$$\frac{T\tan\delta}{c}\Big/\frac{4\pi N\mu^2}{27k}\,\frac{(\epsilon_0+2)^2}{\epsilon_0} = \xi(T) = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2} \qquad \ldots (5)$$

with $\omega\tau_1 = x_1$ and $\omega\tau_2 = x_2$

$$\xi(T) = C_1\frac{x_1}{1+x_1^2} + C_2\frac{x_2}{1+x_2^2} = C_1 f(x_1) + C_2 f(x_2) \qquad \ldots (6)$$

where $$f(x) = \frac{x}{1+x^2}$$

RESULTS

The experimental values of tan δ at different temperature (T) for the different solutions of anisole are given in table I. In the case of solutions of anisole in hexane, benzene and carbon tetrachloride when the curves $\frac{T \tan \delta}{C}$ *vs* T showed maxima, the dipole moments were calculated as usual (Sinha *et al*, 1966) under the assumption of single relaxation time. In all the other cases the values of dipole moments reported in literatures were used for the evaluation of τ values which are included in the tables. Table I also includes the values of $\xi(T)$ calculated from the eqn. (5) in which the observed value of 1.25D was used for μ, the dipole moment of anisole.

DISCUSSION

(a) *Existence of two relaxation times* :

With the help of the τ-values calculated under the assumption of a single relaxation time, graphs of log (τT) against $1/T$ have been drawn for anisole and substituted anisoles. These graphs are shown in figures (1-5). It is seen that the graphs are almost straight lines in the case of all the substituted anisoles, and similar to those observed in the case of molecules with rigid dipole moments (Sinha *et al*, 1965; 1966). But in the case of solutions of anisole in paraffin, hexane, benzene and CCl_4 (figs. 5a-5d) the graphs are *s*-shaped curves. This non-linearity shows that the results are not explicable under the assumption of a single relaxation time for anisole.

From table I it is seen that the values of $\xi(T)$ in the case of solutions in hexane, benzene and CCl_4 at first increase with increase of temperature, then attain a

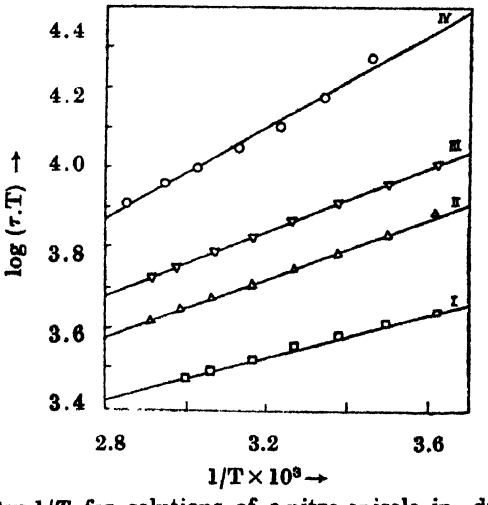

Fig. 1. Plots of log (τT)vs $1/T$ for solutions of *o*-nitro-anisole in different solvents. (τ-in pico-secs) I-*n*-hexane, II-Benzene, III-Carbontetrachloride IV-Paraffin.

TABLE I

Anisole

2.73×10^{-4} moles/cc in hexane				2.73×10^{-4} moles/cc in benzene				2.73×10^{-4} moles/cc in CCl/4				3.64×10^{-4} moles/cc in paraffin			
Temp. °K	tan δ $\times10$	$\tau^*\times10^{12}$ sec.	$\xi(T)$**	Temp. °K	tan δ $\times10$	$\tau^*\times10^{12}$ sec.	$\xi(T)$**	Temp. °K	tan δ $\times10$	$\tau^*10\times^{12}$ sec.	$\xi(T)$**	Temp. °K	tan δ $\times10$	$\tau^*\times10^{12}$ sec.	$\xi(T)$**
276	0.999	5.12	0.404	275	.0761	8.58	0.307	275	.0705	9.40	0.284	297	.0647	14.09	0.211
286	0.977	4.77	0.410	285	.0782	7.71	0.327	285	.0747	8.13	0.311	307	.0688	12.55	0.232
296	0.955	4.10	0.414	295	.0803	6.86	0.347	295	.0767	7.28	0.332	317	.0730	11.18	0.254
306	0.910	3.46	0.408	305	.0823	5.96	0.368	305	.0788	6.40	0.360	329	.0771	9.85	0.279
316	0.868	3.18	0.400	311	.0864	4.10	0.380	311	.0809	5.25	0.378	337	.0792	9.16	0.294
326	0.822	2.94	0 393	319	.0823	3.30	0.385	319	.0830	4.10	0.388	347	.0813	8.41	0.311
336	0.777	2.74	0.383	329	.0782	3.04	0.377	329	.0788	3.35	0.380	355	.0834	7.74	0.325
				339	.0741	2.82	0.368	339	.0747	3.19	0.371				

*Calculated with $\mu = 1.13$D from the graph T tan δ/c vs $1/T$.

*Calculated with $\mu = 1.10$D

*Calculated with $\mu = 1.09$D

*Calculated with $\mu = 1.10$D

**Calculated with $\mu = 1.25$D

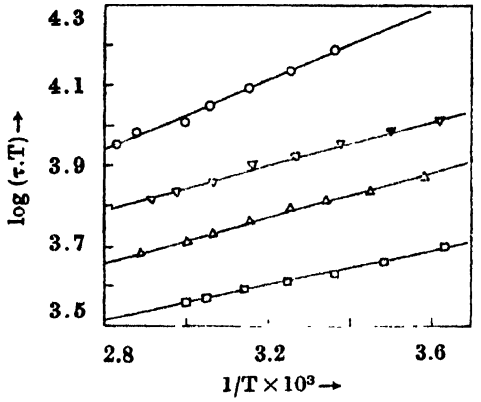

Fig. 2. Plots of $\log(\tau.T)$ vs $1/T$ for solutions of *p*-chloro-anisole in different solvents. (τ-in pico-secs). I-*n*-hexane, II-Benzene, II-Carbon tetrachloride, IV-Paraffin.

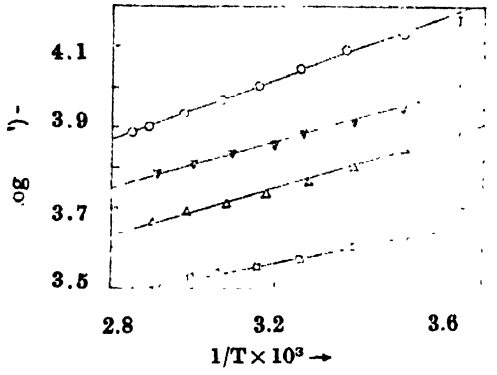

Fig. 3. Plots of $\log(\tau T)$ vs $1/T$ for solutions of *o*-chloro-anisole in different solvents. (τ-in pico-secs). I-*n*-hexane, II-Benzene, III-Carbontotrachloride, IV-Paraffin.

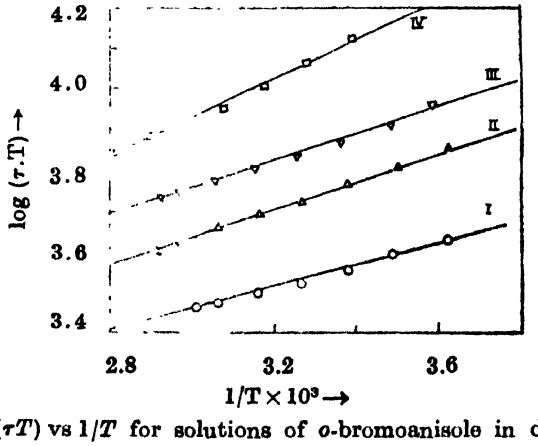

Fig. 4. Plots of $\log(\tau T)$ vs $1/T$ for solutions of *o*-bromoanisole in different solvents. (τ-in pico-secs). I-*n*-hexane, II-Benzene, III-Carbontetrachloride, IV-Paraffin.

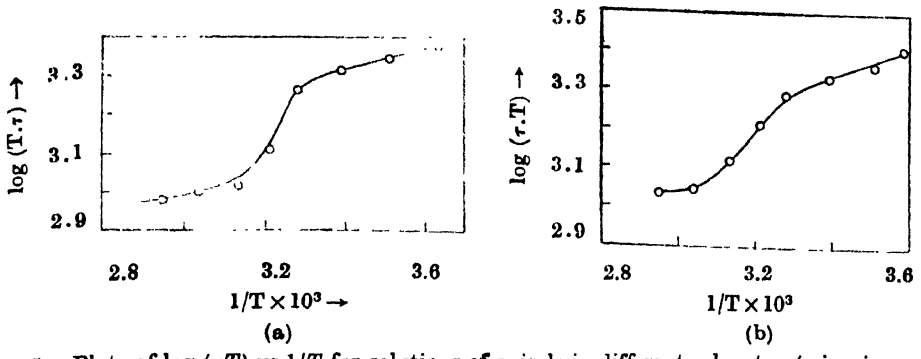

Fig. 5. Plots of log (τT) vs $1/T$ for solutions of anisole in different solvents. (τ in pico-secs).
(a) Benzene, (b) Carbontetrachloride

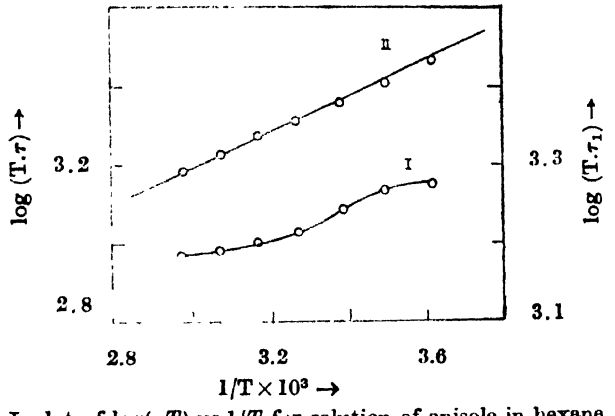

Fig. 5c. Curve I plot of log(τT) vs $1/T$ for solution of anisole in hexane
Curve II. ,, log($\tau_1 T$) vs $1/T$,, ,, ,, (τ and τ_1, in pico-secs)

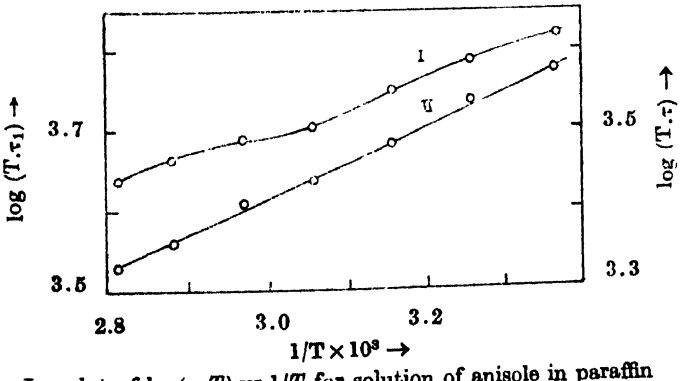

Fig. 5d Curve I. plot of log($\tau_1 T$) vs $1/T$ for solution of anisole in paraffin
Curve II. ,, log (τT) vs $1/T$,, ,, (τ and τ_1 in pico-secs)

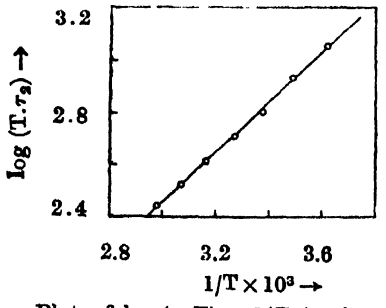

Fig. 5e. Plot of $\log(\tau_2 T)$ vs $1/T$ (τ_2 in pico-secs)

maximum value and finally gradually decrease. The rate of increase of $\xi(T)$ in benzene and CCl_4 solutions is higher than in hexane solution, the rate of decrease being almost the same, in all solutions. In the case of paraffin solution $\xi(T)$ increases monotonously with increase of temperature. All these are shown in fig. 6.

From equation (6) we have

$$\frac{d\xi}{dT} = c_1 \frac{\partial f(x_1)}{\partial T} + C_2 \frac{\partial f(x_2)}{\partial T} \qquad \ldots (7)$$

With $x_1 = \frac{A_1}{T} \exp\left(\frac{V_1}{RT}\right)$ and $x_2 = \frac{A_2}{T} \exp\left(\frac{V_2}{RT}\right)$ (A_1, A_2 are constants, V_1 and V_2 the activation energies per mole for dielectric relaxation of the whole molecule and the methoxy group respectively), eqn. (7) becomes

$$\frac{d\xi}{dT} = \frac{C_1}{T}\left(1+\frac{V_1}{TR}\right)\frac{x_1(x_1^2-1)}{(x_1^2+1)^2} - \frac{C_2}{T}\left(1+\frac{V_2}{TR}\right)\frac{x_2(1-x_2^2)}{(1+x_2^2)^2} \qquad \ldots (7a)$$

At the temperature where $\xi(T)$ is maximum $\frac{d\xi}{dT} = 0$ if the condition $x_1 = 1$ and $x_2 = 1$ holds simultaneously.

In that case $\xi(T)_{max} = \frac{1}{2}(C_1+C_2) = 0.5$

Actually the maximum value of $\xi(T)$ in the case of these solutions (fig. 6) are all less than 0.5 which indicates the presence of more than one relaxation time.

b) *Limits for τ_1 and τ_2.*

Since the condition $x_1 = x_2 = 1$ is not satisfied at the temperature when $\xi(T)$ is maximum it is seen from eqn. (7a) that $\frac{d\xi}{dT}$ at this temperature may be

zero for suitable values of $x_1 > 1$ and $x_2 < 1$ or vice versa. We have assumed the relaxation time for the whole molecule to be greater than τ_2 the relaxa-

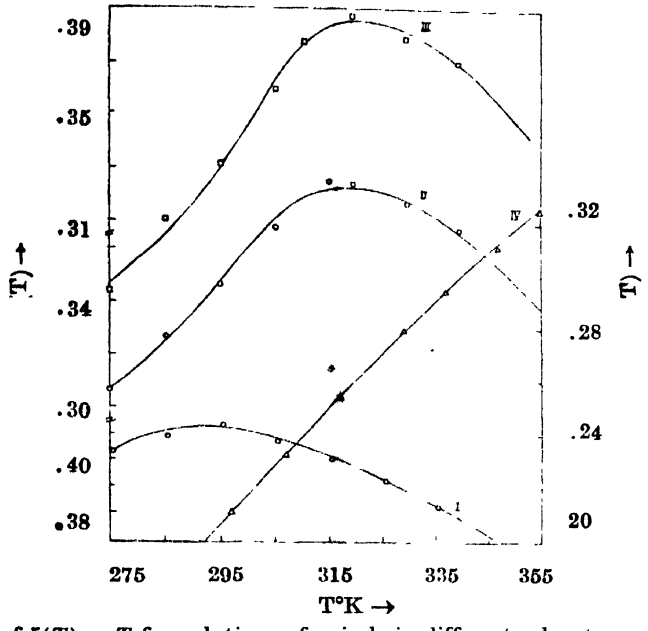

Fig. 6. Plots of $\xi(T)$ vs T for solutions of anisole in different solvents.
I-*n*-hexane, II-Benzene, III-Carbontetrachloride (left-hand side ordinate values)
IV-Paraffin (Righthand side ordinate values)
For curves I, II and III the appropriate ranges for $\xi(T)$ are shown by the broken intervals.

tion time for methoxy group and since $x_1 = \omega\tau_1$ and $x_2 = \omega\tau_2$, $x_1 > x_2$. With $\omega = 2.44 \times 10^{11}$ rad/sec $x_1 > x_2$ means $\tau_1 > 4.1 \times 10^{-12}$ sec and $\tau_2 < 4.1 \times 10^{-12}$ sec.

c) *Determination of the values of* τ_1 and τ_2.

For the determination of the values of τ_1 and τ_2 the analysis of the experimental data of the solutions of anisole has been made on the following considerations :

i) In the same solvent and at the same temperature the value of τ_1 of anisole is very nearly the same as that of a rigid molecule of similar size.

ii) The value of τ_2 (of the methoxy group) is less than 4×10^{-12}sec. for temperatures 296°K and above and becomes equal to 4×10^{-12}sec. at temperatures in between 275°K and 296°K.

Using the value of $\xi(T)$ for hexane solution from table I along with eqn. (6) the following relations are obtained :

$$\xi(276) = C_1 f(x_1) + C_2 f(x_2) = 0.404$$
$$\xi(296) = C_1 f(x_1^1) + C_2 f(x_2) = 0.414 \qquad (8)$$

with $C_1 + C_2 = 1$

For bromobenzene, a molecule having the same size as anisole the values of the relaxation time in hexane solution at temperatures 276°K and 296°K are respectively about 9×10^{-12} and 7×10^{-12} secs. (Sinha *et al*, 1966). The corresponding values of $f(x_1)$ are about 0.37 and 0.42. Assuming that these values also hold for anisole and that the value of τ_2 at 276°K is $\sim4\times10^{-12}$ sec i.e. $f(x_2)\approx0.5$ the insertion of these values in the first expression of equation (8) gives $.37C_1+.5C_2 = .403$ whence $C_1\sim0.7$ and $C_2\sim0.3$. Using these values of C_1 and C_2 in the second relation of equation (8) the value of $f(x^1_2)$ at 296°K comes out to be 0.4 approximately i.e. $\tau_2\sim2\times10^{-12}$sec. In this way the values of τ_1 and τ_2 at all temperatures have been determined approximately. Afterwards, the values of C_1, C_2, τ_1 and τ_2 have been slightly adjusted so that the calculated $\xi(T)$ values are in satisfactory agreement with the experimental values of $\xi(T)$ at the corresponding temperatures and the plots of $\log(\tau_1T)$ vs $1/T$ and $\log(\tau_2T)$ vs $1/T$ yield good straight line graphs. The τ_1- and τ_2-values are given in table II and the graphs are shown in figs 5(c) and 5(e). The hindering potential energies V_1 and V_2 calculated from the graphs in the usual way are given at the foot of the Table. Once the valuess of τ_2 at different temperatures have been determined, the calculation of τ_1-values in paraffin solution become much simplified. The final values of τ_1 calculated with $C_1 = 0.9$ and $C_2 = 0.1$ are given in table III and the graph of $\log(\tau_1T)$ vs $1/T$ is shown in fig. 5(d). The value of the potential barrier V_1 obtained from the graph is given along with the Table.

Solution	C_2	t%
Hexane	0.3	38.7
Paraffin	0.1	12.9

In tables II and III the values of the time of relaxation of bromobenzene at different temperatures in hexane and paraffiin solutions respectively have been included for comparison. It is seen that in each case the τ_1-values of anisole are comparable with those of bromobenzene, a molecule having the same size as that of anisole.

Now an estimate of the percentage of molecules capable of relaxation by the processes of rotation of the molecule as a whole of the methoxy group is made by using the relation $C_2 = t(\mu_2/\mu)^2$. Putting $\mu = 1.25$D and $\mu_2 = 1.10$D (Hase, 1953; Fisher, 1954) the following values of t are obtained :

The small value of $C_2 = 0.1$ in paraffin solution indicates that in this case most of the anisole molecules relax by the process of the rigid rotation of the whole molecule and consequently, the plot of $\log(\tau.T)$ vs $1/T$ (obtained by using the τ-values calculated under the assumption of a single relaxation time) shows only small departure from linearity fig 5b.

TABLE II

Anisole in hexane

$C_1 = 0.7$ $C_2 = 0.3$

Temperature	$\tau_2 \times 10^{12}$ sec	$\tau_1 \times 10^{12}$ sec	$\tau \times 10^{12}$ sec Bromobenzene
276	4.06	9.80	8-50
286	2.99	8.94	7.60
296	2.16	8.04	6.96
306	1.68	7.42	6.25
316	1.31	6.85	5.45
326	1.03	6.27	
336	0.82	5.82	

$V_2 = 4.33$K.Cal/Mole, $V_1 = 1.00$K.Cal/Mole

TABLE III

Anisole in Paraffin

$C_1 = 0.9$ $C_2 = 0.1$

Temperature	$\tau_1 \times 10^{12}$ sec	$\tau \times 10^{12}$ sec Bromobenzene
297	20.1	19.96
307	17.8	17.14
317	15.2	15.09
329	13.3	13.33
337	12.1	11.79
347	10 5	10.67
355	9.6	

$V_1 = 2.2$K.Cal/Mole

In the case of hexane solution $C_2 = 0.3$ and the plot of $\log(\tau T)$ vs $1/T$ (fig. 5c) shows greater deviation from linearity. Such deviations are still more pronounced in the case of solutions in benzene and in CCl_4 and may therefore indicate greater values of C_2 in the two cases.

Analysis of the data (in terms of the τ_2-values so determined) in the case of solutions in benzene and CCl_4 has not been very successful. However, it may be noted that the maximum value of $f(x_2) = 0.5$ in the case of benzene and CCl_4 solutions should occur at temperatures well beyond the temperatures at which $\xi(T)$ is maximum in the respective cases i.e. between 275°K and 305°K. If we assume that in the case of solution in benzene $f(x_2)$ is max. at about 295°K, the value of τ_2 at this temperature will be 4×10^{-12}sec. which agrees well with the values of 4.4×10^{-12}sec. in benzene solution at 25°C (Fisher, 1954) and 4.6×10^{-12}sec. reported by Hase (1953) at 25°C in other solvents. Further experiments are being

conducted to obtain complete information about τ_2 the relaxation time of the methoxy group in anisole in different environments.

d) *Substituted anisoles*

It can be seen from figs. 1-4 that the graphs of log $(\tau.T)$ vs $1/T$ in the case of the solutions of *o*-chloro-, *o*-bromo-, *o*-nitro- and *p*-chloroanisoles in all the solvents are all straight lines similar to those observed in the case of molecules with rigid dipoles and having a single relaxation time (Sinha *et al*, 1966). It, therefore, suggests that the molecules of these substituted anisoles relax predominantly by the process of rotation of the molecule as a whole. Considerations of the expected values of C_2 for these compounds also lend support to this idea. For, if the value of t for the different compounds in less viscous solvents is taken to be 40% then from the relation $C_2 = t.\ (\mu_2/\mu)^2$ it is seen that as the value of μ of the substituted anisoles varies from 2.5D for the halo substituted anisoles to 4.8D for ortho nitroanisole, the values of C_2 come out to be about 0.1 for the former compounds and .025 in the latter compound. It may, therefore, be concluded that, the contributions to the dielectric loss in these cases are mainly due to the rotation of the molecule as a whole.

It may be noted here that in the case of solution of *p*-chloroanisole in Nujol Grubb and Smyth (1961) reported very high values of τ_1 for the rotation of the molecule as a whole. The τ_1-values are very large compared with those for molecules of similar sizes and may have resulted from an attempt to interpret the observed results in terms of two relaxation times.

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